

ELECTRODIALYSIS REVERSAL (EDR) FOR PERCHLORATE TREATMENT

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INTRODUCTION

A new analytical method developed by the California Department of Health Services (CDHS) in April 1997 decreased the perchlorate detection limit from 400 µg/L to 4 µg/L (Okamoto, et al., 1997), resulting in perchlorate detection in many drinking water sources. Recent detection of perchlorate and lack of treatment information is cause of concern for many water utilities. Based on existing health effects data, California has established an action level of 18 µg/L for perchlorate (CDHS, 1997). Regulatory levels in other states and USEPA have not been established. However, perchlorate is listed for USEPA regulatory review.

Magna Water Company in Utah provides potable water to the northwest sections of Salt Lake County. The groundwater in one of their well fields has shown detectable levels of perchlorate and concentrations are expected to rise due to contaminant plume migration. Due to current cost and potential future cost escalation of purchased water as well as the general need to protect and utilize available water resources, it is desirable to maintain use of these well fields.

Currently available treatment options for perchlorate are discussed in light of Magna source water quality and treatment requirements. Preliminary results of pilot testing of the most prominent candidate process, electrodialysis reversal (EDR), and cost estimates for a range of source water perchlorate concentrations and finished water quality goals are presented.

BACKGROUND

At conditions typical of drinking water treatment, perchlorate exists as a monovalent anion (ClO₄). It exhibits limited sorption and negligible volatilization potential (Catts and McCullough, 1997). Chemically similar to nitrate, treatment alternatives for perchlorate are also similar. Table 1 summarizes perchlorate treatment options and associated issues in general and with regards to Magna.

Kinetic constraints limit the effective application of chemical reduction, and current commercially available alternatives include:

- Biological reduction through processes similar to denitrification
- Ion exchange using nitrate-specific resin
- Membrane desalting technologies; *i.e.*, reverse osmosis (RO), nanofiltration (NF), and electrodialysis reversal (EDR)

Biological reduction, while effective and appropriate for wastewater applications, has several drawbacks for drinking water treatment. First, the process requires that a carbon source be added to the water, potentially leading to elevated microbial substrate availability or other impairment of the finished water quality. Second, operating a biological process in a drinking water application poses potential problems from a public acceptance perspective. In addition, biological reduction of perchlorate occurs under anoxic conditions and production of sulfides and other reduced compounds could be problematic. Finally, in general, biological reduction tends to be less stable and lacks the reliability of physical/chemical processes.

Ion exchange can be quite effective for perchlorate removal. However, Magna well water has elevated concentrations of total dissolved solids (TDS) (approximately 1300 mg/L) limiting the feasibility of direct application of ion exchange at Magna. Membrane desalting technologies offer reliable treatment of perchlorate-contaminated drinking water. In general, RO/NF would be cost competitive with EDR. However, with silica concentrations of approximately 80 mg/L, recovery would be unacceptably low (on the order of 50%). However, silica is not concentrated by EDR, and silica levels have no impact on EDR recovery. While perchlorate removal by EDR would be expected to correspond to other anions with similar charge density (e.g. nitrate) no data was available when this study was initiated.

In light of the above discussion, specific objectives of this study were:

- Perform a characterization of water quality at Magna to confirm treatment process selections
- Determine rejection characteristics of perchlorate by EDR
- Develop conceptual designs and cost estimates for a range of EDR staging and implementation options

• Evaluate feasibility and cost implications for ion exchange

TABLE 1

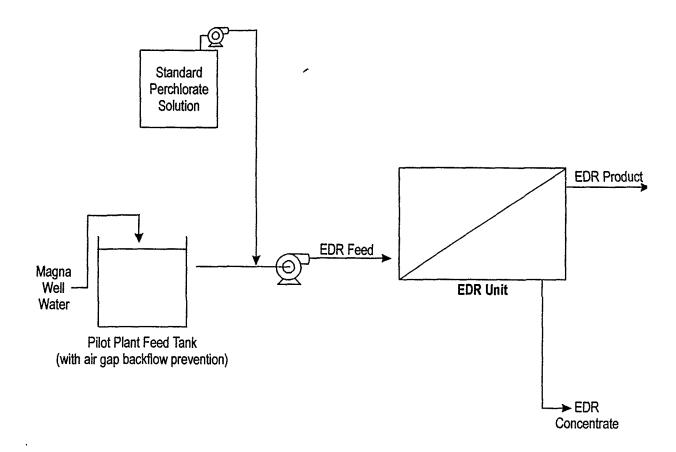
COMPARISON OF POTENTIAL PERCHLORATE TREATMENT PROCESSES

Process	Advantage	Limitations
Chemical Reduction - With bisulfite or reduced common metals		• Too slow for ex situ treatment
Electrochemical Reduction - Reduction of perchlorate occurs at anode	Well understoodNo toxic by-products	 High capital and O&M costs Electrolysis of water Safety Not proven for drinking water applications
Biochemical Reduction - Enzymes from perchlorate-reducing bacteria purified and used as heterogeneous or homogeneous catalyst	Fast reactionHigh efficiency	 Enzyme identification, production, and extraction is expensive Difficult implementation Not commercially available Not proven
Biological reduction - Similar to biological denitrification	 Fast reaction Possible to achieve in existing biofilters 	 Regulatory/public acceptance Process stability Unproven for drinking water applications High capital and O&M costs (potentially)
Ion Exchange - Similar to nitrate removal	Reasonable cost (in general)Easy implementation	 Waste disposal Resin life TDS (in particular sulfate) competition limits applicability at Magna
Membranes - RO/NF/EDR	 High removal efficiency Low cost Easy implementation Promising preliminary results 	 Waste disposal Elevated silica limits RO/NF applicability at Magna

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APPROACH

EDR pilot testing was conducted to evaluate perchlorate removal and confirm design criteria for EDR treatment of the Magna groundwater. Figure 1 shows a process flow diagram of the pilot system.



EDR PILOT STUDY PROCESS FLOW DIAGRAM

Figure 1

The EDR pilot unit was an Ionics Aquamite III, generally characterized by the following attributes:

- 7.4 gpm production capacity operating at 70% recovery
- Two electrical stages and four hydraulic stages with Mark IV spacers
- Contained in 20 feet long by 8 feet wide by 10 feet high standard shipping container
- The container includes a feedwater tank, feedwater pump, multimedia filter, 10 micron cartridge filter, chemical feed systems, and a product water tank.

Feed water for the pilot system was taken from an uncontaminated production well. Perchlorate was added using an ammonium perchlorate stock solution, and testing was conducted at various feed concentrations as indicated in Table 2.

TABLE 2
EXPERIMENTAL CONDITIONS FOR EDR PILOTING

Duration (Weeks)	Operating Conditions	Objectives
1	 Set-up EDR Performed preliminary runs Ran during day only for 4 days Continuous operation began June 7, 1999 	 Started up system Verified proper performance of system components Performed operation, maintenance, and sampling training
5	• Dosed perchlorate to achieve 130 μ g/L in EDR feed	 Obtained baseline perchlorate removal data Collected data for ion exchange evaluations
4	• Dosed perchlorate to achieve $60\mu g/L$ in EDR feed	Monitored for concentration dependent perchlorate removal rate
3	• Dosed perchlorate to achieve 15 μ g/L in EDR feed	 Quantified perchlorate removal after extended period of operation Evaluated low level removal performance
2	Discontinued perchlorate dosing	• Monitored for perchlorate release from EDR membranes
1	Demobilization	Collected membrane samples for analysisPrepared unit for return shipment

Daily monitoring included the following parameters: pH, conductivity, temperature, pressure, flow rate, voltage and current. Samples of feed, product, and brine were collected weekly and analyzed for TDS, Chlorine, sulfate, and perchlorate. The EDR process model was verified using pilot data and used to evaluate a range of full-scale conditions. Ion exchange treatment was considered using the Calgon ISEP ion exchange process model.

RESULTS

Table 3 summarizes raw water quality parameters. The groundwater quality at Magna is quite stable and variability in feed water characteristics was minimal during testing.

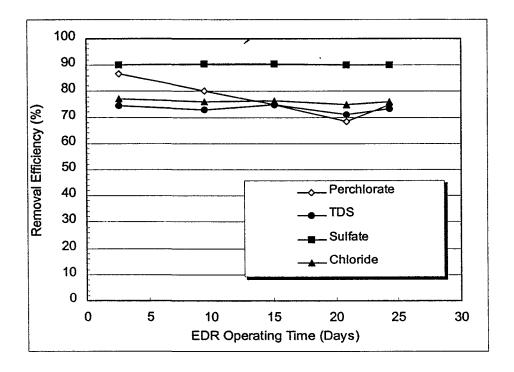
TABLE 3
TYPICAL WELL WATER QUALITY

Parameter	Value
TOC (mg/L)	1.10
UV 254 (cm ⁻¹)	0.020
pH	<u> </u>
Temperature (°C)	16
Turbidity (NTU)	0.12
Total Alkalinity (mg/L as CaCO ₃)	390
Hardness (mg/L as CaCO ₃)	520
Manganese (mg/L)	0.066
Iron (mg/L)	0.069
TDS (mg/L)	1300

Figures 2, 3, and 4 show perchlorate, chloride, sulfate, and TDS removal efficiency when perchlorate was dosed at 130, 160, and 15 μ g/L, respectively. TDS, sulfate, and chloride exhibited relatively constant removal efficiency over the entire study period. Perchlorate removals decreased from 87%, initially, to percent removals in the low 70s (Figures 2 and 3). Perchlorate removals appeared to stabilize in this range for the following three weeks of operating time. The decrease in perchlorate dosing level from 130 μ g/L to 60 μ g/L did not impact percent removals (Figure 3). However, perchlorate removals dropped to about 60% before returning to the low-to-mid 70s, following the decrease in dosing level from 60 μ g/L to 15 μ g/L (Figure 4). Moreover, brine concentrations were higher than expected for a two to three week period following this change (data not shown).

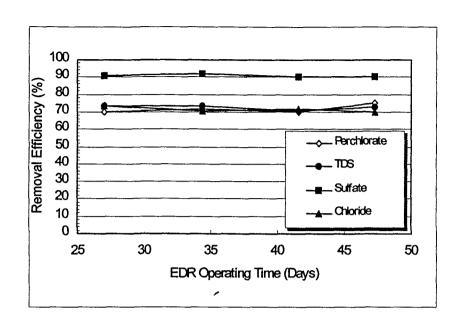
The membranes in the EDR stack were constructed from ion exchange resin material. Perchlorate has a reasonably high affinity for certain ion exchange resins. Therefore, the higher perchlorate

removal efficiency at the start of the study (Figure 2) may have been because removals occurred by two mechanisms: ion exchange and EDR operation. As the ion exchange capacity of the membranes became exhausted, removals decreased to that which could be achieved solely by EDR operation. The observed decrease in performance following the change from dosing 60 μ g/L to 15 μ g/L was likely caused by the desorption of perchlorate from the EDR membranes, as a new equilibrium was established at the lower perchlorate concentrations. The drop from 130 μ g/L to 60 μ g/L was apparently insufficient to cause observable changes in the perchlorate removal efficiency. The phenomena of sorption and desorption of perchlorate is expected to be more important in the brine stream due to the greater concentrations of anions which compete for ion exchange sites. Therefore, these phenomena are not expected to be of concern for product water concentrations, unless influent perchlorate concentrations are highly variable with rapid changes in feed concentrations.



REMOVAL EFFICIENCY OF PERCHLORATE AND OTHER IONS (DOSING 130 μ g/L PERCHLORATE)

Figure 2



REMOVAL EFFICIENCY OF PERCHLORATE AND OTHER IONS (DOSING 60 μ g/L PERCHLORATE)

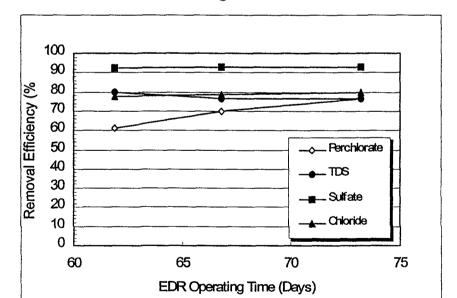


Figure 3

REMOVAL EFFICIENCY OF PERCHLORATE AND OTHER IONS (DOSING 15 μ g/L PERCHLORATE)

Figure 4

A process model was used to extend these pilot-scale results to evaluate several full-scale configurations. Table 4 summarizes removal efficiencies for perchlorate and other anions for systems comprised of two to four stages. Table 5 lists equipment, construction, annual operation and maintenance, and overall production cost estimates for each system configuration using a design feed flow rate of 5mgd and average production flow rates of 3.45 mgd for 2 stages, 3.0 mgd for 3 stages, 2.8 mgd for 4 stages.

TABLE 4

REMOVAL EFFICIENCY FOR VARIOUS EDR SYSTEM CONFIGURATIONS

	Removal Efficiency (%)		
	2-Stage	3-Stage	4-Stage
Perchlorate	71	88	94
Sulfate	84	93	97
Chloride	81	91	96
TDS	75	88	94

TABLE 5
EDR FACILITY COST ESTIMATES

Cost	2-Stage	3-Stage	4-Stage
EDR Equipment (\$)	3,591,000	4,481,000	6,190,000
Capital (\$)	7,850,000	9,175,000	11,765,000
Annual O&M (\$/Yr)	658,000	590,000	682,000
Production (\$/kgal)	1.16	1.20	1.41

Ion exchange system design criteria and construction costs tend to be relatively insensitive to the feed water perchlorate concentration and the finished water perchlorate goal, when used as a polishing system. For a 5 mgd system to be added after at least two stages of EDR, equipment cost is approximately \$3,000,000 and the total capital cost is \$4,600,000. As background ionic strength increases, regeneration requirements and operational costs increase. Table 6 lists ion exchange system and production costs for a range of EDR staging conditions.

TABLE 6
ION EXCHANGE POLISHING COST ESTIMATES

Pretreatment	2-Stage EDR	3-Stage EDR	4-Stage EDR
Ion Exchange Equipment (\$)	3,000,000	3,000,000	3,000,000
Ion Exchange Capital* (\$)	4,600,000	4,600,000	4,600,000
Ion Exchange Annual O&M (\$/year)	390,000	300,000	240,000
Ion Exchange Production (\$/kgal)	0.81	0.71	0.62
EDR Production (\$/kgal)	1.16	1.20	1.41
Total Production (\$/kgal)	1.97	1.91	2.03

^{*} Note that the capital cost for ion exchange polishing excludes equipment and facilities included in the EDR facility. Capital cost for a stand-alone ion exchange facility would be greater than a polishing application.

SUMMARY AND CONCLUSIONS

Results of pilot testing indicate that, for the water quality observed at Magna, EDR provides effective removal of perchlorate and the removal efficiency of perchlorate is similar to that of chloride. Some sorption of perchlorate to the EDR ion exchange membranes appeared to occur, although this effected brine perchlorate concentrations to a much greater extent than the product water.

Unless very high perchlorate removal is required, additional stages of EDR provides a more cost effective alternative that ion exchange polishing. Should ion exchange polishing be required, 3-stage EDR appears to provide optimal pretreatment based on economic considerations.

REFERENCES

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Okamoto, H.S., D. K Rishi, W.R. Steebe, F.S. Baumann, and S. K. Pesern. Using Ion Chromatography to Detect Perchlorate. Source AWWA, 91(10):73.